

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>C04B 41/83, F16J 15/10</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 98/09926</b> <b>(43) International Publication Date:</b> 12 March 1998 (12.03.98)
<b>(21) International Application Number:</b> PCT/GB97/02275 <b>(22) International Filing Date:</b> 26 August 1997 (26.08.97) <b>(30) Priority Data:</b> 9618377.7                      3 September 1996 (03.09.96)                      GB <b>(71) Applicant (for all designated States except US):</b> FLEXITAL- LIC LIMITED [GB/GB]; P.O. Box 21, Rochdale OL12 7EU (GB). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> HOYES, John, Robert [GB/GB]; 2 The Brook, Calderbrook Road, Littleborough OL15 9NW (GB). STANCLIFFE, Alan [GB/GB]; 87 High- croft Way, Syke, Rochdale, Lancashire OL12 9UE (GB). <b>(74) Agents:</b> SHERRARD-SMITH, Hugh et al.; Appleyard Lees, 15 Clare Road, Halifax, West Yorkshire HX1 2HY (GB).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the</i> <i>claims and to be republished in the event of the receipt of</i> <i>amendments.</i>
<b>(54) Title:</b> STRENGTHENED GRAPHITE SHEET MATERIAL		
<b>(57) Abstract</b>  A strengthened exfoliated graphite sheet material and a method for making same is described. The method comprises the steps of applying at least one coat of a liquid plastics material to at least one face of said exfoliated graphite sheet material and drying said at least one liquid coat to leave an adherent plastics material sheet on said graphite sheet material.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon	KR	Republic of Korea	PL	Poland		
CN	China			PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

- 1 -

STRENGTHENED GRAPHITE SHEET MATERIAL

The present invention relates to graphite sheet material having improved strength and handlability.

5

Exfoliated or expanded graphite may be compressed to form sheet material which finds many applications in sealing gaskets for example owing to its high compressibility and conformability. However, exfoliated  
10 graphite sheet is relatively very brittle, easily fracturing when bent or roughly handled. Various exfoliated graphite sheet materials having improved strength and durability have been proposed. GB2154675 of common ownership herewith describes an expanded graphite  
15 web material having a reinforcing core of thin metal, the material being made by laminating a sheet of expanded graphite to each face of a thin metal, e.g. nickel, sheet by adhesive means. The tensile strength of the resulting graphite sheet is greatly increased. Another proposal has  
20 involved the bonding by adhesive means of a plastics material sheet film to one or both faces of a graphite sheet.

Whilst these earlier proposals have resulted in  
25 exfoliated graphite sheet having greatly improved strength and durability, they suffer from the disadvantage of being costly to manufacture due, inter alia, to the requirement of needing expensive capital equipment for their production. Furthermore, when a plastics sheet is bonded  
30 to graphite sheet the sheet must be at a minimum thickness to enable the sheet to be passed through rollers and applied to the graphite. Thus when the gasket is clamped between two flanges and subject to heat, as in a cylinder head gasket, the plastics will stick to the flange. This

- 2 -

results in the flange having to be cleaned when the gasket has to be replaced. This is costly and time consuming.

5 It is an object of the present invention to provide exfoliated graphite sheet having greatly improved strength and resistance to handling damage compared to ordinary exfoliated graphite sheet, at an economic cost and to provide a method for its production.

10 According to a first aspect of the present invention, there is provided strengthened exfoliated graphite sheet material, said exfoliated graphite sheet material having on at least one face thereof a sheet of a plastics material applied initially as a liquid.

15 According to a second aspect of the present invention, there is provided a method of strengthening exfoliated graphite sheet material, the method comprising the steps of applying at least one coat of a liquid  
20 plastics material to at least one face of said exfoliated graphite sheet material and drying said at least one liquid coat to leave an adherent plastics material sheet on said sheet material.

25 The term "plastics material" used herein is intended to include any suitable polymer and/or synthetic resin or mixture thereof capable of being applied to the graphite sheet in liquid form. The liquid form may be in the form of a monomer, in melt form or in solution in a solvent for  
30 example.

The plastics material sheet may be applied by any suitable method including spraying, brushing, dipping and by electrophoretic methods for example.

35

- 3 -

The plastics material sheet may be applied in several coats to one or both faces of the graphite sheet material as desired. When more than one coat is applied, each coat may be dried prior to application of the next or alternatively, more than one coat may be dried at a time so long as the total coating is self supporting without running off the sheet surface for example. The number of coats applied will be dependent upon the final desired thickness and strength of the plastics material sheet and the desired degree of enhancement of strength of the graphite sheet.

Depending upon the plastics material being applied, it may also be necessary to further include a curing step in addition to or as part of the drying step. The curing step may be to polymerise the dried coating and increase the strength of the plastics material coating itself. The temperature at which drying and/or the curing steps will be carried out will be dependent upon the type of plastics material in question.

Where more than one coat of plastics material is applied these may not necessarily all be of the same material.

The thickness of each individual plastics material layer may be controlled to an extent by the viscosity of the applied liquid coat, the greater the viscosity, the thicker each coat may be.

An example of a suitable plastics material may be a water based acrylic polymer resin.

Two or more coats of plastics material may be applied. It has been found that depending upon the

- 4 -

density of the graphite sheet and physical and chemical characteristics of the applied liquid, the first coat tends to penetrate the graphite structure and act as a sealant, whereas a second coat tends to remain substantially completely on the surface due to the sealing effect of the first coat. The strengthening effect of the second coat and any further coats are, therefore, further enhanced. However, it is possible by control of liquid viscosity to minimise penetration of the graphite structure so as to allow the use of a single coat only. Other techniques to prevent penetration such as the addition of fillers to the liquid or the use of anti-wetting agents may also be employed.

However, it may be desirable to achieve penetration of the graphite with a sealing coating so as to improve adhesion of a second coat to the first coat and also to the graphite itself by virtue of deeper penetration of the graphite porosity. Control of the depth of penetration may be controlled inter alia by viscosity of the first coating.

Where the graphite sheet is to be used for gasket applications, it may be further treated so as to provide gasket release properties, i.e. easy removal from surfaces which have been sealed. This may be achieved either by additional surface coating on top of the plastics material coating or by addition of suitable agents to the liquid plastics coating material. In the former case additional surface coatings may comprise polytetrafluoroethylene (PTFE), silicones for example. In the latter case, diluents or agents such as silicones, matting agents, fillers such as silica or ground up minerals such as china clay, and, antioxidants for example may be used. The plastics to filler ratio may be, by volume, less than or

- 5 -

equal to 10:1 or less than or equal to 5:1 or in the region of 4:1.

Strengthened exfoliated graphite sheet according to the present invention is suitable for the manufacture of so-called spiral wound gaskets and also for the protection of already formed spiral wound gaskets by coating thereof. The plastics material coating prevents the edges of exfoliated graphite sheet material from being friable and easily chipping, either during cutting or during subsequent handling and storage.

The surface of the graphite material itself may be treated for example by indenting or shallow spiking or by chemical means so as to improve the mechanical bonding of the resulting plastics material to the surface.

In order that the present invention may be more fully understood, examples will now be described by way of illustration only.

Exfoliated graphite sheet of thickness about 1mm was selected for testing. This material would fracture across its width when bent through a relatively small angle of about 10 to 20°.

Three different self-crosslinking acrylic resin emulsions were chosen for their differing physical characteristics. These were :

Revacryl 274 (trade name) - soft, flexible Tg -24°C  
Revacryl 275 (trade name) - tough, flexible Tg -5°C  
Revacryl 277 (trade name) - tough, stiff Tg +10°C

- 6 -

Each emulsion was coated by spraying on to the graphite sheet in 1 and 2 coats and bend tests carried out as specified below :

5		<u>Bend Test</u>
	Revacryl 274, 1 coat	40°
	Revacryl 274, 2 coats	90°
	Revacryl 275, 2 coats	90°
	Revacryl 277, 2 coats	90°**
10	** This coating material was superior to the others and enabled the graphite sheet to be repeatedly bent through 180° without fracturing.	

15 The samples coated with Revacryl 277 were also completely tack-free at room temperature and the coated graphite material easily cut with scissors without chipping of the edge.

20 Revacryl 277 may include plastics such as PTFE, china clay in powder form, water and a dispersing agent such as Dispex N40. The ratio of plastics to china clay by volume may be less than or equal to 10:1 or 5:1 and is preferably in the region of 4:1. Such substance may be difficult or impossible to make as a sheet standing by itself and being  
25 able to be handled. However, when on the graphite, the sheet has sufficient strength to allow the graphite to be bent. Furthermore, the Revacryl 277 does not tend to stick to flanges and in any event this sheet has less plastics per unit area than a layer that is applied in the  
30 form of a sheet thus allowing easy replacement of gaskets.

The reader's attention is directed to all papers and documents which are filed concurrently with or previous to this specification in connection with this application and  
35 which are open to public inspection with this



- 7 -

specification, and the contents of all such papers and documents are incorporated herein by reference.

5 All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive.

10 Each feature disclosed in this specification (including any accompanying claims, abstract and drawings), may be replaced by alternative features serving the same, equivalent or similar purpose, unless expressly  
15 stated otherwise. Thus, unless expressly stated otherwise, each feature disclosed is one example only of a generic series of equivalent or similar features.

20 The invention is not restricted to the details of the foregoing embodiment(s). The invention extends to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any  
25 method or process so disclosed.

- 8 -

CLAIMS

1. A method of strengthening exfoliated graphite sheet material, the method comprising the steps of applying at  
5 least one coat of a liquid plastics material to at least one face of said exfoliated graphite sheet material and drying said at least one liquid coat to leave an adherent plastics material sheet on said sheet material.
- 10 2. A method according to Claim 1 wherein the plastics material sheet is applied by a technique selected from the group comprising spraying, brushing, dipping and by electrophoretic methods.
- 15 3. A method according to either Claim 1 or Claim 2 further including a curing step for the plastics material.
4. A method according to Claim 3 wherein the curing step is included as part of the drying step.  
20
5. A method according to any one preceding claim from 1 to 4, wherein if more than one sheet of plastics material is applied these are not all of the same material.
- 25 6. A method according to any one of preceding claims 1 to 5 and further including the step of including a release agent.
7. A method according to claim 6, wherein said release  
30 agent is included in said liquid plastics material.
8. A method as claimed in any preceding claim in which the liquid penetrates the graphite.

- 9 -

9. A method as claimed in any preceding claim comprising adding filler to the liquid prior to applying the coat of plastics material.
- 5 10. A method of making a strengthened graphite sheet material substantially as hereinbefore described with reference to the accompanying description and examples.
- 10 11. Strengthened exfoliated graphite sheet material, said exfoliated graphite sheet material having on at least one face thereof a sheet of a plastics material applied initially as a liquid.
- 15 12. A strengthened graphite sheet material according to claim 11 wherein said plastics material is a water-based acrylic polymer resin.
- 20 13. A strengthened graphite sheet material according to either claim 11 or claim 12 further including a release agent.
- 25 14. A strengthened graphite sheet material according to claim 13 wherein said release agent is provided as a separate outer layer.
15. A strengthen graphite sheet material according to claim 13 wherein said release agent is incorporated into said plastics material sheet.
- 30 16, A strengt6hene graphite sheet material according to claim 1 or any one of claims 11 to 15 wherein porosity adjacent the surface of the graphite material is impregnated with the plastics material.

- 10 -

17. A strengthened graphite sheet material according to any of claims 11 to 16 in which the plastics includes a filler.
- 5 18. A strengthened graphite sheet material according to claim 17 in which the ratio by volume of plastics to filler is less than or equal to 10:1 or less than or equal to 5:1 or in the region of 4:1.
- 10 19. A strengthened graphite sheet material as claimed in any of claims 11 to 18 in which the sheet material is in the form of a spiral.
- 15 20. A strengthened graphite sheet material substantially as hereinbefore described with reference to the accompanying description and examples.

# INTERNATIONAL SEARCH REPORT

In. tional Application No

PCT/GB 97/02275

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C04B41/83 F16J15/10

According to International Patent Classification(IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X  A	PATENT ABSTRACTS OF JAPAN vol. 014, no. 342 (C-0743), 24 July 1990 & JP 02 124768 A (HITACHI CHEM CO LTD), 14 May 1990, see abstract -& DATABASE WPI Section Ch, Week 9025 Derwent Publications Ltd., London, GB; Class E36, AN 90-189654 XP002050298 see abstract  --- -/--	1-5,8, 10,11, 16,20  12

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

16 December 1997

Date of mailing of the international search report

09/01/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Rosenberger, J

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 97/02275

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X  A	PATENT ABSTRACTS OF JAPAN vol. 015, no. 173 (C-0828), 2 May 1991 & JP 03 040910 A (NIPPON KASEI KK), 21 February 1991, see abstract -& DATABASE WPI Section Ch, Week 9114 Derwent Publications Ltd., London, GB; Class A82, AN 91-097647 XP002050299 see abstract ---	1,2, 5-11,13, 15-18,20  12
X  Y	DE 43 32 346 A (GOETZE AG) 30 March 1995  see claims 1,4 see column 2, line 30 - line 35 ---	1-6,8, 10,11, 13,14, 16,20 19
Y  A	EP 0 519 620 A (UCAR CARBON TECHNOLOGY CORP) 23 December 1992  see claims 1,4 see column 1, line 1 - line 31 -----	19  1,11,12

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 97/02275

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 4332346 A	30-03-95	NONE	
EP 0519620 A	23-12-92	US 5198063 A	30-03-93
		DE 69222472 D	06-11-97
		JP 6024872 A	01-02-94

Form PCT/ISA/210 (patent family annex) (July 1992)

**THIS PAGE BLANK (USPTO)**